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Synthesis, Structure and Spectroscopy of a New Dinuclear Iron–Sulfur Compound $(Et_4N)_2[Fe_2(1,2\text{-}OSC_6H_4)_4]\cdot 2CH_3CN$

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Abstract

A new dinuclear pentacoordinate iron–sulfur compound $(Et_4N)_2[Fe_2(1,2\text{-}OSC_6H_4)_4]$ (1) was synthesized and the structure of $1\cdot 2CH_3CN$ was determined to be monoclinic, $P2_1/n$, $M_r = 950.97$, with crystal data $a = 11.580(2)$, $b = 16.731(6)$, $c = 12.869(2)$ Å; $\beta = 98.07(2)°$, $V = 2468.6$ Å^3, $Z = 2$, $D_x = 1.279$ g cm^{-3}. From the 2242 independent reflections with $I \geqslant 3\sigma(I_o)$, the final R converged to 0.069. The centrosymmetric anion of 1 is a dimer of $[Fe(mp)_2]^-$ bridged by the alkoxy groups of the two bridging mp^{2-}. The atom Fe(III) is in a distorted trigonal bipyramidal environment with O(1) and O(2) as the two apical atoms and O(1′)S(1)S(2) forming the equatorial plane. Both ^1H NMR and CV measurements in DMSO and CH_3CN showed the existence of species $D(CH_3CN)$ or M(DMSO), respectively, from the equilibrium (1). The dissociation of 1 into M in strongly polar solvent is further evidenced by ^1H NMR in DMF of intermediate polarity, which gave a ratio of D:M = 8:1. Mössbauer effect measured at 77 K indicated that the ground state spin of Fe(III) in $1\cdot 2CH_3CN$ is 5/2.

Iron–sulfur compounds have been synthesized and studied extensively due to their relevance to naturally occurring iron–sulfur proteins. Among those, five-coordinate iron–sulfur compounds with 1,2-dithiolato ligands have been richly reported, e.g., $[Fe_2(S_2C_2H_4)_4]^{2-}$ [1], $[Fe_2(S_2C_2(CO_2(CH_3)_2)_4]^{2-}$ [2], $[Fe_2(S_2C_2(CF_3)_2)_4]^{1-,0}$ [3–5], $[Fe_2(S_2C_2Ph_2)_4]^{2-}$ [4, 5], $[Fe_2(S_2C_6H_4)_4]^{2-}$ [6] and $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$ [7]. All these compounds are dimercapto bridged and some have an interesting chemistry [4, 7]. On the other hand, similar five-coordinate dinuclear iron(III)–sulfur compounds with dialkoxy bridges are scarce. It will be beneficial to the comparison of oxo and thio bridges if the related compound $(Et_4N)_2[Fe_2(1,2\text{-}OSC_6H_4)_4]$ (1, $C_6H_4OS^{2-} = mp^{2-}$) can be synthesized and studied. Here we report the preparation, ^1H NMR, Mössbauer and cyclic voltammogram of 1 and the X-ray structure of $1\cdot 2CH_3CN$.

Under anaerobic conditions in Schlenk apparatus, a solution of 1.0 g (6.15 mmol) of anhydrous $FeCl_3$ in 20 ml of absolute ethanol was added dropwise to a stirred solution of 2.64 g (15.5 mmol) of Na_2-mp (H_2mp: *o*-mercaptophenol, obtained from sodium metal and H_2mp in a 2:1 molar ratio) and allowed to react for 30 min at room temperature. The reaction mixture was filtered and a solution of Et_4NBr in absolute ethanol was added to the filtrate. The black microcrystalline product that separated immediately was collected and recrystallized from CH_3CN at 60 °C. On filtration and drying *in vacuo*, the yield was 58% (based on Fe). *Anal.* Calc. for $Fe_2S_4O_4C_{44}H_{62}N_4$: Fe, 11.75; S, 13.49. Found: Fe, 12.18; S, 13.51%. ν(KBr): 578, 570 (Fe–O); 385, 340 (Fe–S) cm^{-1}. Compound $1\cdot 2CH_3CN$ is soluble in polar solvents and showed a smoky black color in CH_3CN but was dark green in DMF and DMSO, indicating that different species are present in these solvents.

Crystals of $(Et_4N)_2[Fe_2(mp)_4]\cdot 2CH_3CN$ are monoclinic, space group $P2_1/n$, with $a = 11.580(2)$, $b = 16.731(6)$, $c = 12.869(2)$ Å, $\beta = 98.07(2)°$, $V = 2468.6$ Å^3, $Z = 2$, $D_x = 1.279$ g cm^{-3}. Diffraction data of a single crystal were collected in the range of $1 \leqslant \theta \leqslant 25$ on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å).

A total of 4704 independent reflections, of which 2242 had $I \geqslant 3\sigma(I_o)$, corrected for Lp factors as well as for empirical absorption were used for structure determination by an SDP program pack on a PDP 11/70 computer.

The structure was solved by the heavy atom method and successfully refined in the space group $P2_1/n$. The position of the Fe atom was provided by a Patterson map. Repeated least-squares refinements and difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Final full-matrix least-squares refinements with anisotropic thermal vibrations of all non-hydrogen atoms (isotropic temperature factors of atoms in the solvated molecule CH_3CN) converged to $R(R_w) =$

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TABLE I. Selected Atomic Distances (Å) and Bond Angles of the Compound $(Et_4N)_2[Fe_2(mp)_4]\cdot 2CH_3CN$

Fe–Fe′	3.165(2)	C(7)–C(8)	1.376(9)
Fe–S(1)	2.313(2)	C(7)–C(12)	1.400(9)
Fe–S(2)	2.296(2)	C(8)–C(9)	1.402(10)
Fe–O(1′)	2.017(3)	C(9)–C(10)	1.433(14)
Fe–O(1)	2.064(4)	C(10)–C(11)	1.35(2)
Fe–O(2)	1.913(4)	C(11)–C(12)	1.361(14)
S(1)–C(2)	1.762(6)	N–C(20)	1.514(6)
S(2)–C(8)	1.775(7)	N–C(30)	1.498(7)
O(1)–C(1)	1.342(6)	N–C(40)	1.513(7)
O(2)–C(7)	1.301(8)	N–C(50)	1.510(7)
C(1)–C(2)	1.385(8)	C(20)–C(21)	1.497(8)
C(1)–C(6)	1.384(8)	C(30)–C(31)	1.521(10)
C(2)–C(3)	1.396(8)	C(40)–C(41)	1.511(9)
C(3)–C(4)	1.383(10)	C(50)–C(51)	1.504(9)
C(4)–C(5)	1.345(10)	C(13)–C(14)	1.434(13)
C(5)–C(6)	1.383(9)	C(14)–N(2)	1.129(14)
S(1)–Fe–S(2)	117.60(7)	S(2)–Fe–O(2)	88.2(2)
S(1)–Fe–O(1)	83.6(1)	O(1)–Fe–O(1′)	78.3(2)
S(1)–Fe–O(1′)	122.7(1)	O(1)–Fe–O(2)	175.8(2)
S(1)–Fe–O(2)	97.5(2)	O(1′)–Fe–O(2)	97.8(2)
S(2)–Fe–O(1)	94.9(1)	Fe–O(1)–Fe	101.7(2)
S(2)–Fe–O(1′)	117.8(1)		

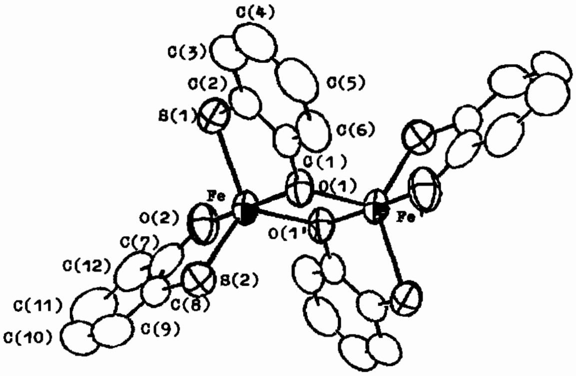

Fig. 1. Structure of the $[Fe_2(mp)_4]^{2-}$ anion.

0.069 (0.077). In crystals of $1\cdot 2CH_3CN$ discrete anions of 1 are separated by tetraethylammonium cations. The cation features the expected structural properties and calls for no special comment.

Selected bond distances and bond angles are listed in Table I. Figure 1 depicts the structure of the anion of 1 which is centrosymmetric. The center of symmetry falls on the crystallographic center of symmetry. The oxygen atoms of two mp^{2-} correlate two five-coordinate Fe atoms while the two sulfur atoms form terminal Fe–S bonds. Each iron atom has another mp^{2-} as a bidentate terminal ligand. The Fe–O(1) bond within $[Fe(mp)_2]^{1-}$ is 0.047 Å longer than the Fe–O(1′) bond connecting two $[Fe(mp)_2]^{1-}$. The average value of $Fe–O_b$ (2.041 Å) is longer than inorganic oxobridges in $[\mu\text{-}O(Fe(salen))_2]$ (1.78 Å) [8] and $[\mu\text{-}O(FeCl_3)_2]^{2-}$ (1.734 Å) [9] and is closer to alkoxy bridges in $[Fe(salpa)Cl]_2$ (1.96 Å) [10] or $[Fe(salen)Cl]_2$ (2.078 Å) [11]. The terminal Fe–O(2) bond (1.913 Å) is shorter than six-coordinate $Fe–O_t$ ($[Fe(acac)_3]$, 1.992 Å [12]; $[Fe(cat)_3]^{3-}$, 2.02 Å [13]) but longer than four-coordinate $Fe–O_t$ ($[Fe(OR)_4]^-$, R = 2,4,5,6-Me_4C_6H, 1.847 Å [14]; R = 2,4,6-$Cl_3C_6H_2$, 1.86 Å [14]) and close to five-coordinate $Fe–O_t$ in [Fe(salen)Cl] [15] and $[\{Fe(salen)\}_2O]$ [8] (1.88 ~ 1.92 Å). These bond length comparisons indicate that when the formal oxidation level of Fe is 3+, the Fe–O bond increases with increase of coordination number.

The FeO(1)O(1′)O(2)S(1)S(2) unit is a distorted trigonal bipyramid with O(1), O(2) as the two apical atoms and O(1′)S(1)S(2) forming the equatorial plane. Since Fe–O(1) is longer than Fe–O(2), the Fe atom is pushed toward O(2) on the same side of the equatorial plane 0.177 Å away. The FeO(2)S(2)C(7)C(8) ring is planar but the other five-membered FeO(1)S(1)C(1)C(2) ring is not, with the Fe atom 0.503 Å out of plane. The two phenyl rings related to one Fe atom are nearly perpendicular to one another (dihedral angle 100.2°) in contrast to those in the anion $[Fe_2(S_2C_6H_4)_4]^{2-}$ which are parallel (dihedral angle 10.05° [6]). This difference could be a result of different hybridization of bridging atoms sp^2(O) *versus* sp^3(S). The participation of vacant d orbitals of S during hybridization has also been proposed [16].

^1H NMR data (DMSO-d_6: −36.0, 23.9, −48.0 ppm; DMF-d_7: α, −22, 18.5, −40; β, −34, 26, −48 ppm; $\alpha/\beta = 8$, CD_3CN: −22, 18.5, −40 ppm) indicate different species existing in solvents of different polarity. According to equilibrium (1) between dimer (**D**) and monomer (**M**)

$$\underset{\mathbf{D}}{[Fe_2(mp)_4]^{2-}} + 4\text{solv.} \rightleftharpoons \underset{\mathbf{M}}{2[Fe(mp)_2(solv)_2]^-} \qquad (1)$$

complete dissociation into **M** was observed for **1** in DMSO and undissociated in CD_3CN. Both **D** and **M** were present in the ratio of 8:1 in DMF. Such results agree with the polarity sequence of DMSO > DMF > CH_3CN. The isotropic shifts of these species either in the solid state or in solution are mainly contact in origin; when antiferromagnetic coupling occurs in the dimer $[Fe_2(mp)_4]^{2-}$ (μ_{Fe} = 5.28 BM), the isotropic shifts of ^1H in CD_3CN move toward the central field as expected.

Mössbauer spectrum measured at 77 K gave δ = 0.407 mm/s, ΔE_Q = 1.179 mm/s corresponding to $S = 5/2$ ground state spin for Fe(III).

Cyclic voltammograms also showed the dissociation of **D** into **M** in strongly polar solvents. Compound **1** gave one reversible redox couple at $E_{1/2}$ = −0.92 V (DMSO) or $E_{1/2}$ = −0.84 V (DMF) *versus*

SCE in the range of 0 ~ 2.0 V corresponding to the reaction

$$[Fe_2(mp)_4]^{2-} \overset{sol}{\rightleftharpoons} 2[Fe(mp)_2(sol)_2]^{-} \underset{2e}{\overset{2e}{\rightleftharpoons}} 2[Fe(mp)_2(sol)_2]^{2-}$$

Two irreversible reduction waves at $E_{p,c(1)} = -0.94$ V and $E_{p,c(2)} = -1.59$ V were observed in CH_3CN corresponding to the reaction

$$[Fe_2(mp)_4]^{2-} \xrightarrow{e} [Fe_2(mp)_4]^{3-} \xrightarrow{e} [Fe_2(mp)_4]^{4-}$$

Supplementary Material

Listings of positional parameters and temperature factors, of complete bond lengths and angles as well as of least-square planes are available from the author on request.

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